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<b>(21) International Application Number:</b> PCT/AU96/00314 <b>(22) International Filing Date:</b> 24 May 1996 (24.05.96) <b>(30) Priority Data:</b> PN 3234 30 May 1995 (30.05.95) AU PN 7263 22 December 1995 (22.12.95) AU <b>(71) Applicant (for all designated States except US):</b> SOLA INTERNATIONAL HOLDINGS LTD. [AU/AU]; Sherriffs Road, Lonsdale, S.A. 5160 (AU). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> TOH, Huan, Kiak [MY/AU]; 24 Medway Street, Fullerton, S.A. 5063 (AU). BATEMAN, Ian, Roger [AU/AU]; 6 Charlson Rise, Happy Valley, S.A. 5159 (AU). DIGGINS, David, Robert [AU/AU]; 2 Ruby Court, Flagstaff Hill, S.A. 5159 (AU). CIESLINSKI, Bohdan, Grzegorz [AU/AU]; 2 Bethany Court, Noarlunga Downs, S.A. 5168 (AU). <b>(74) Agent:</b> PHILLIPS ORMONDE & FITZPATRICK; 367 Collins Street, Melbourne, VIC 3000 (AU).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HIGH INDEX/HIGH ABBE NUMBER COMPOSITION		
<b>(57) Abstract</b>  A cross-linkable polymeric casting composition including an effective amount of A: an acrylic or methacrylic monomer which provides high rigidity and low colour dispersion (High Abbe number) to the final product; B: a di- or polythio compound; C: a di- or polyvinyl monomer, and optionally D: a polymerisable comonomer.		

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HIGH INDEX/HIGH ABBE NUMBER COMPOSITION

The present invention relates to the manufacture of plastic optical articles such as video discs and ophthalmic lenses.

The most widely used plastic ophthalmic lens material is polymerised diethylene glycol bis (allyl carbonate). This polymer has proved a satisfactory material for the manufacture of ophthalmic lenses because of a combination of features, including excellent transmission, resistance to discolouration, high strength and high impact resistance. The material has a reasonable abrasion resistance and can be coated to improve that resistance.

Lenses formed from polymers including divinyl benzene are generally brittle and have a high yellowness index.

In Australian Patent Application 81216/87, the entire disclosure of which is incorporated herein by reference, applicant describes a cross-linkable casting composition including at least polyoxyalkylene glycol diacrylate or dimethacrylate and at least one poly functional unsaturated cross-linking agent. Whilst the lenses produced from the prior art compositions provide advances in the art, difficulties may be encountered in certain applications. For example, difficulties may be encountered in some patients in fitting lenses made from such compositions. Eye discomfort, including eye fatigue problems, may be encountered. Moreover, such lenses have been found to be cosmetically unattractive.

Further, in Australian Patent Application 75160/91, the entire disclosure of which is incorporated herein by reference, applicant describes a polyoxyalkylene glycol diacrylate or dimethacrylate; a monomer including a recurring unit derived from at least one radical-polymerisable bisphenol monomer capable of forming a homopolymer having a high refractive index of more than 1.55; and a urethane monomer having 2 to 6 terminal groups selected from a group comprising acrylic and methacrylic groups.

Japanese Patent Application 63-309509 to Showa Denko KK discloses the formation of a prepolymer of divinyl benzene and a polythiol compound which may be used in the formation of optical materials with high refractive indexes.

Japanese Patent Application 63-19498 to Mitsubishi Gas discloses a high

refractive index composition of divinyl benzene and a thiol compound. However optical lenses produced thereby exhibit unacceptable strain characteristics and cure times.

However, there remains a need in the prior art for optical articles of very  
5 high refractive indexes, high Abbe number, high rigidity, very low densities and excellent colour, that still retain excellent mechanical properties.

Accordingly, it is an object of the present invention to overcome, or at least alleviate, one or more of the difficulties related to the prior art.

Accordingly, the present invention provides a cross-linkable polymeric  
10 casting composition including an effective amount of  
an acrylic or methacrylic monomer which provides high rigidity and low colour dispersion (High Abbe number) to the final product;  
a di- or polythio compound;  
a di- or polyvinyl monomer; and optionally  
15 a polymerisable comonomer.

The casting composition may be heat and/or UV-curable.

The optical article formed from the casting composition of the present invention may exhibit a refractive index in the high to very high -index range, high Abbe number, low density and high rigidity.

20 By the term "high refractive index", as used herein, we mean a polymer having a refractive index of at least approximately 1.55, preferably 1.57. By the term "very high refractive index" as used herein, we mean a polymer having a refractive index of approximately 1.59 or above, preferably 1.60 or above.

By the term "low density", as used herein, we mean a density in the range  
25 of approximately 1.15 to 1.25 g cm<sup>-3</sup>.

By the term "Abbe number", as used herein, we mean the number expressing the extent to which the shorter and longer wavelengths of light are separated by refraction through a lens, that is the amount the lens disperses the various colours. The greater the number, the smaller the dispersion. The Abbe  
30 number may be calculated utilising the following formula:

$$V = \frac{n_D - 1}{n_F - n_C}$$

where

$n$  = refractive index

$D$  = 589.3 nm (sodium) yellow

$F$  = 486.1 nm blue green

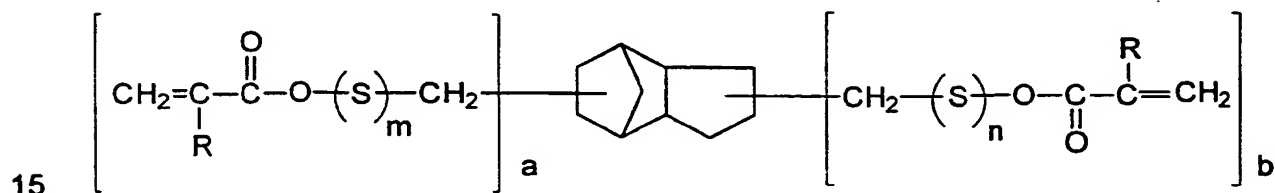
5  $C$  = 656.3 nm red

By the term "high Abbe number" as used herein, we mean a polymer having an Abbe number of at least approximately 35, preferably 38 or above.

By the term "high rigidity" as used herein, we mean a polymer having a glass transition temperature ( $T_g$ ) of at least approximately 65°C, preferably approximately 70°C, more preferably approximately 75°C or above.

The acrylic or methacrylic monomer (Component A) may be selected from acrylates or methacrylate derivatives of a cycloolefin. An acrylate or methacrylate derivative of tricyclodecane is preferred.

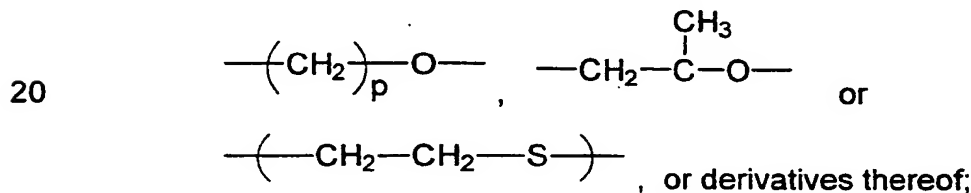
The acrylate or methacrylate derivative may be of the formula:



where R can be H or CH<sub>3</sub>

$a = 1-3$ ,  $b = 1-3$ ,  $m = 0-6$ ,  $n = 0-6$ .

S is a spacer group selected from one or more of the following

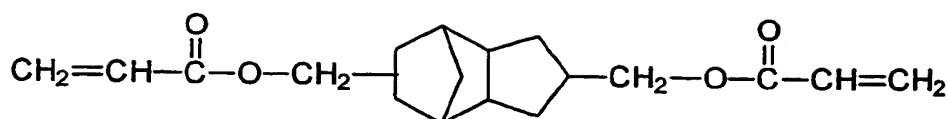


wherein  $p = 1-4$

A tricyclodecane dimethanol diacrylate or methacrylate is preferred.

A tricyclodecane dimethanol diacrylate or diacryloyl oxymethyl tricyclodecane of the following formula is preferred.

4



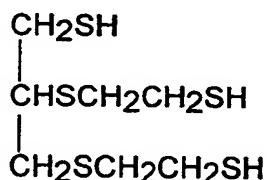
(DCPA)

The acrylic or methacrylic monomer may alternatively or in addition be selected from highly rigid, high Abbe No. polyfunctional acrylates or methacrylates. Pentaerythritol tetracrylate (PTA) is a preferred example.

- 5 The acrylic or methacrylic monomer (Component A) may be present in amounts sufficient to provide high Abbe number and high rigidity, but not so much as to cause brittleness or low tintability. Amounts of from approximately 20 to 60% by weight, preferably approximately 30 to 55% by weight, more preferably approximately 35 to 45% by weight, based on the total weight of the casting composition have been found to be suitable.
- 10

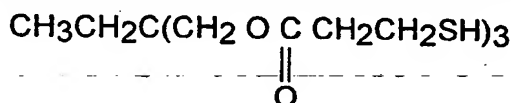
The di- or polythiol compound (Component B) may be of any suitable type. A di-, tri- or tetra polythiol compound may be used. A tri- or tetra-polythiol is preferred. The thiol may be selected from one or more of the following:

- (a) 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol [MDO]

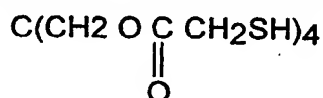


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- (b) Trimethylolpropane Tris (3-mercaptopropionate) [TTMP]

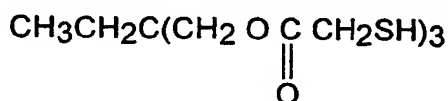


- (c) Pentaerythritol Tetrakis (3-mercaptopropionate) [PTMA]



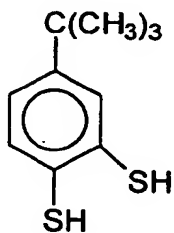
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- (d) Trimethylolpropane Tris (3-mercaptopropionate) [TTMA]



5

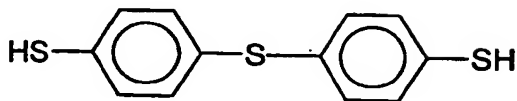
- (e) 4-t-butyl-1,2-benzenedithiol



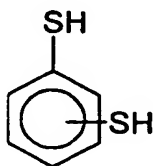
- (f) Bis-(2-mercaptoethyl)sulfide



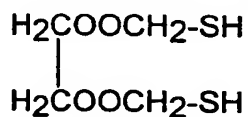
- 5 (g) 4,4'-thiodibenzenethiol



- (h) benzenedithiol

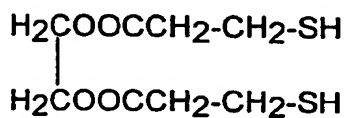


- (i) Glycol Dimercaptoacetate

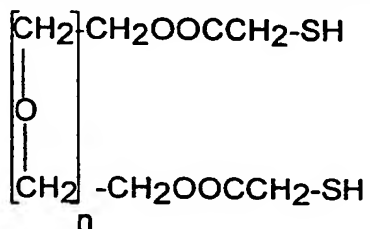


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- (j) Glycol Dimercaptopropionate Ethylene bis(3-Mercaptopropionate)

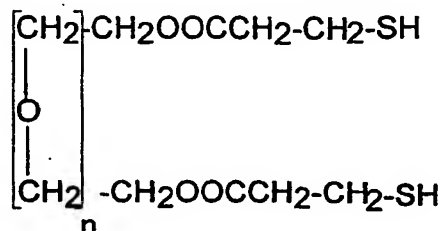


- (k) Polyethylene Glycol Dimercaptoacetates

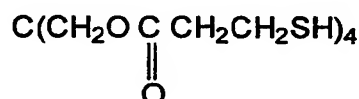


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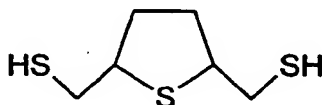
- (l) Polyethylene Glycol Di(3-Mercaptopropionates)



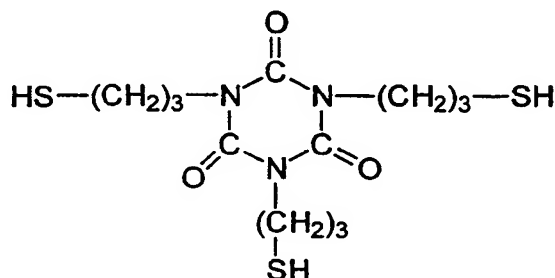
- (m) Pentaerythritol Tetrakis (3-mercapto-propionate) [PTMP]



- 5 (n) Mercapto-methyl tetrahydrothiophene [MMTHT]



- (o) Tris-(3-mercaptopropyl)isocyanurate [TMPIC]

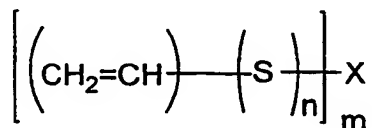


4-mercaptomethyl-3,6-dithia-1,8-octanedithiol [MDO] is particularly preferred.

- 10 The di- or polythiol compound (Component B) may preferably be present in amounts of from approximately 15 to 60% by weight, more preferably approximately 20 to 55% by weight and particularly about 25 to 45% by weight based on the total weight of the casting composition.

- 15 The inclusion of a divinyl or polyvinyl monomer (Component C) provides a reduction in flexibility, and thus an increase in hardness in optical articles produced therefrom.

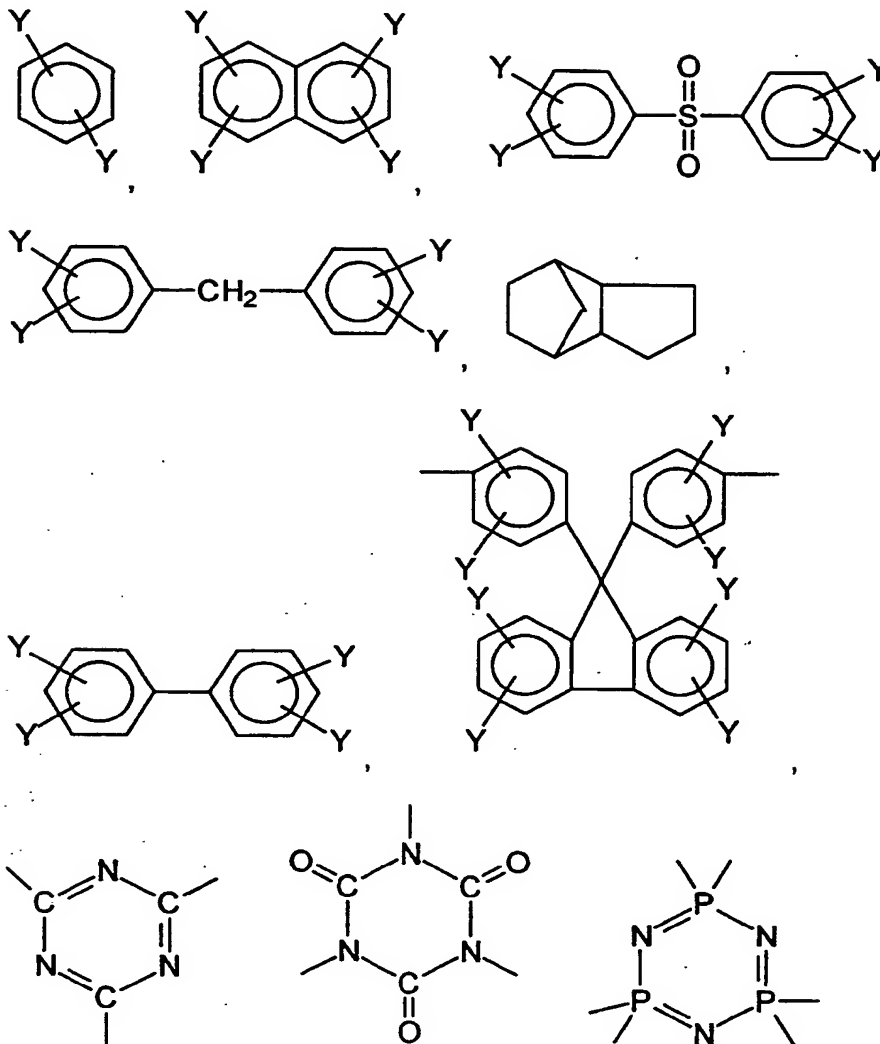
The divinyl or polyvinyl monomer may be a rigid cyclic vinyl monomer. Component C may have the following formula:





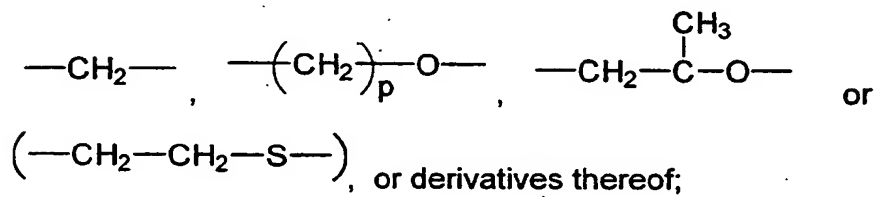
wherein

X is selected from one or more of the following



5

S is a spacer group selected from one or more of the following



10

Y is hydrogen or halogen

n = 0, 1 or 2

m = 2 - 6

p = 1 - 4

The divinyl or polyvinyl monomer may be a di- or tri- vinyl monomer. An aromatic divinyl is preferred. The aromatic divinyl monomer may include divinyl  
5 benzene, divinyl naphthene or derivatives thereof. 1,5-divinyl naphthene may be used. Divinyl benzene is particularly preferred.

The divinyl or polyvinyl monomer may preferably be present in amounts sufficient to provide rigidity and high index in optical articles formed from the casting composition, but not so much as to cause brittleness or low tintability.  
10 Amounts of from approximately 5 to 50% by weight, preferably approximately 15 to 40% by weight, more preferably about 20 to 30% by weight based on the total weight of the casting composition are preferred.

The cross-linkable polymeric casting composition may optionally further include a polymerisable comonomer (Component D).

15 The polymerisable comonomer may be selected to improve the properties and/or processability of the cross-linkable polymeric casting composition. The polymerisable comonomer may be selected to improve tint rate, hardness, abrasion resistance and the like of the resulting polymer. The polymerisable comonomer may be an unsaturated or epoxy comonomer. The polymerisable  
20 comonomer may be selected from any suitable type, e.g. methacrylates, acrylates, vinyls, vinyl ethers, allyls, epoxides, and the like.

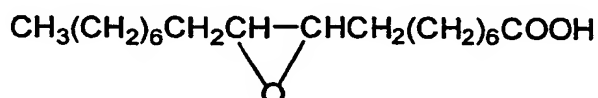
The polymerisable comonomer may preferably be selected from one or more of epoxidised monomer or oligomer vinyls, allylics, polyoxyalkylene glycol di-, tri-, tetra- and higher acrylates or methacrylates, polymerisable bisphenol  
25 monomers, urethane monomers having 2 to 6 terminal acrylic or methacrylic groups, fluorene acrylates or methacrylates, and thioacrylate or thiomethacrylate monomers.

Where an epoxidised monomer or oligomer is included, the epoxidised monomer may function to improve curing and casting characteristics. The  
30 epoxidised monomer or oligomer may fall into one or more of the following classes: internal, terminal, mono-functional, di-functional, tri-functional, tetra-functional, aliphatic, aromatic, cyclic, structurally simple, structurally complex,

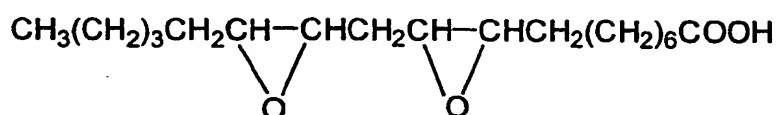
esters, ethers, amines. An epoxidised soybean material may be used. The epoxidised monomer or oligomer may be selected from one or more of the following

- 1) Epoxidised soybean oil - Triglycerides of a mixture of epoxidised a) oleic acid, b) linoleic acid, c) linolenic acid

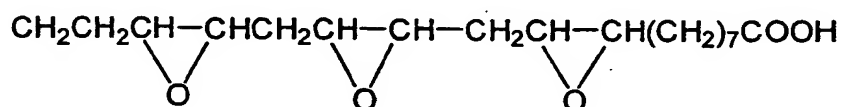
a)



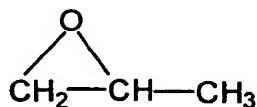
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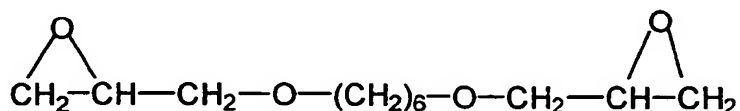
c)



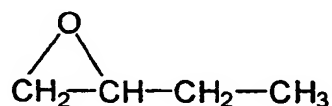
- 2) Propylene Oxide



- 3) Hexanediol diglycidyl ether (HDGE)

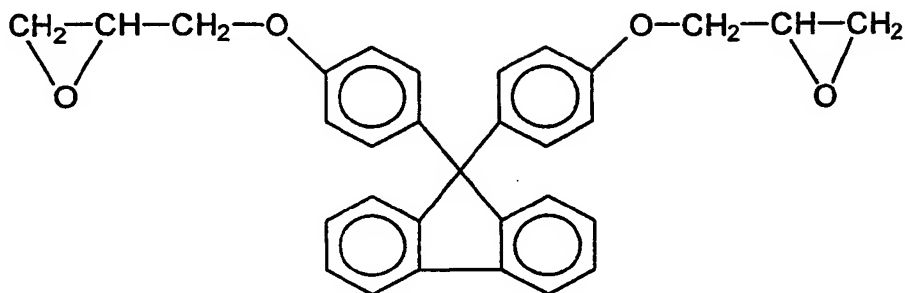


- 4) 1,2 epoxy butane

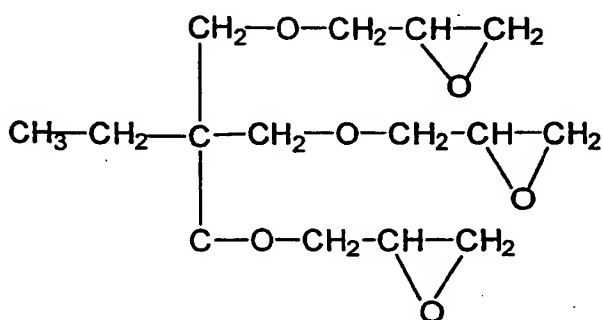


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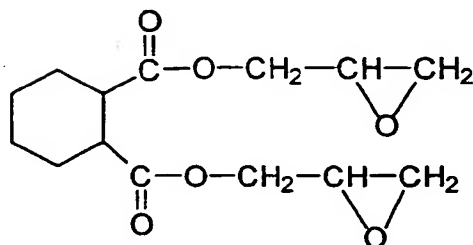
## 5) Bisphenol fluorene diglycidyl ether (BPGE)



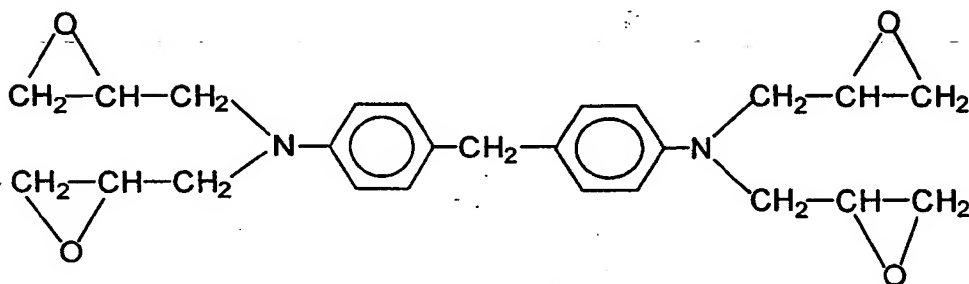
## 6) Epolight 100MF



## 5 7) AK-601



## 8) MY 721



10 The epoxidised monomer may be present in amounts of from approximately 0.001% to 10% by weight, preferably 0.01% to 5%, more preferably approximately 0.01% to 2%, based on the total weight of the casting composition.

Where a vinyl comonomer is included, the vinyl comonomer may be selected from styrene, substituted styrenes, 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (DTU), a divinyl ester monomer of a bi- or polycyclic compound and mixtures thereof. The divinyl ester monomer of a bi- or polycyclic  
5 compound may be of the type described in copending provisional patent application entitled "UV Curable High Index Vinyl Esters" to Applicants, the entire disclosure of which is incorporated herein by reference.

The vinyl comonomers may be present in amounts of from 0 to approximately 20% by weight, preferably approximately 5 to 15% by weight,  
10 based on the total weight of the casting composition.

Where a thiodiacrylate or dimethacrylate is included, the thiodiacrylate or dimethacrylates may be selected from bis(4-methacryloylthioethyl)sulfide (BMTES) and bis(4-methacryloylthiophenyl)sulfide (BMTS). The thioacrylate or methacrylate may be present in amounts of from 0 to approximately 20% by  
15 weight, preferably approximately 5 to 15% by weight, based on the total weight of the casting composition.

Where a fluorene diacrylate or dimethacrylate is included, the fluorene diacrylate or dimethacrylate monomer may be selected from a bisphenol fluorene dihydroxy acrylate (BFHA) or a bisphenol fluorene dimethacrylate (BFMA) or  
20 mixtures thereof.

The fluorene diacrylate or dimethacrylate monomer may be present in amounts of from 0 to approximately 20% by weight, preferably approximately 1 to 10% by weight.

The polyoxy alkylene glycol diacrylate or dimethacrylate compound  
25 according to the present invention, when present, may include ethylene oxide or propylene oxide repeating units in its backbone. A polyethylene glycol dimethacrylate is preferred. Suitable materials include dimethylacrylates where the number of repeating ethylene oxide groups is between 4 and 14. Suitable materials include those sold under the trade names NK Ester 4G, 6G, 9G or 16G.  
30 A 9G monomer is preferred.

The polyoxy alkylene glycol diacrylate or dimethacrylate component may be present in amounts of from 0 to approximately 20% by weight, preferably

approximately 5% to 15% by weight, based on the total weight of the casting composition.

The high index bisphenol monomer component in the cross-linkable casting composition when present may be selected from: dimethacrylate and diacrylate esters of bisphenol A; dimethacrylate and diacrylate esters of 4,4'-bishydroxy-ethoxy-bisphenol A and the like.

Preferred high index bisphenol compounds include bisphenol A ethoxylated dimethacrylate and tetra brominated bisphenol A ethoxylated dimethacrylates. A bisphenol A ethoxylate dimethacrylate sold under the trade designation ATM 20 by Ancomer has been found to be suitable.

The high index bisphenol monomer may be present in amounts of from 0 to approximately 20% by weight, preferably 5 to 15% by weight based on the total weight of the casting composition.

The cross-linkable casting composition according to the present invention may include a polymerisation curing agent.

The polymerisation curing agent may be a radical heat cationic or radical initiator. A radical heat initiator is preferred. The compositions may be cured by a combination of UV radiation and heat.

The amount of curing agent may vary with the monomers selected. It has been possible to operate with a relatively low level of curing agent of between approximately 0.05 and 1.5%, preferably 0.4% to 1.0% by weight.

The following curing agents have been found to be suitable.

- AIBN (Azo radical heat initiator)  
Azodiisobutyronitrile
- Trigonox TX-29 (Dialkyl Peroxide radical heat initiator)  
1,1-di-(*n*-butyl peroxy-3,3,5-trimethyl cyclohexane)
- TBPEH (Alkyl Perester radical heat initiator)  
t-butyl per-2-ethylhexanoate
- (Diacyl Peroxide radical heat initiator)  
Benzoyl Peroxide
- (Peroxy Dicarbonate radical heat initiator)  
Ethyl Hexyl Percarbonate

- (Ketone Peroxide radical heat initiator)  
Methyl ethyl ketone peroxide
- Cyracure UV1-6974 (cationic photoinitiator)  
Triaryl sulfonium hexafluoroantimonate
- 5 - Lucirin TPO (radical photoinitiator)  
2,4,6-Trimethylbenzoyldiphenylphosphine oxide
- Vicure 55 (radical photoinitiator)  
methyl phenylglycoxylate
- Bis(t-butyl peroxide) diisopropylbenzene
- 10 - t-butyl perbenzoate
- t-butyl peroxy neodecanoate
- Amicure DBU
- Amicure BDMA
- DABCO
- 15 - Amicure DBU and/or Amicure BDMA are preferred.

Initiator may be a single component or combination of initiator components.

- Other additives may be present which are conventionally used in casting compositions such as inhibitors, dyes, UV stabilisers and materials capable of
- 20 modifying refractive index. Mould release agents may be added. Such additives may include:

UV Absorbers including

- Ciba Geigy Tinuvin P - 2(2'-hydroxy-5'methyl phenyl) benzotriazole
- Cyanamid Cyasorb UV 531 -2-hydroxy-4-n-octoxybenzophenone
- 25 - Cyanamid Cyasorb UV5411-2(2-hydroxy-5-t-octylphenyl)- benzotriazole
- Cyanamid UV 2098 - 2 hydroxy-4-(2-acryloyloxyethoxy) benzophenone
- National Starch and Chemicals Permasorb MA - 2 hydroxy-4-(2 hydroxy-3-methacryloxy)propoxy benzophenone
- Cyanamid UV24 - 2,2'-dihydroxy-4-methoxybenzophenone
- 30 - BASF UVINUL 400 - 2,4 dihydroxy-benzophenone
- BASF UVINUL D-49 - 2,2'-dihydroxy-4,4' dimethoxy- benzophenone
- BASF UVINUL D-50 - 2,2', 4,4' tetrahydroxy benzophenone

- BASF UVINUL D-35-ethyl-2-cyano-3,3-diphenyl acrylate
- BASF UVINUL N-539-2-ethylhexyl-2-cyano-3,3-diphenyl acrylate
- Ciba Geigy Tinuvin 213

Hindered amine light stabilisers (HALS), including

- 5
- Ciba Geigy Tinuvin 765/292 - bis (1,2,2,6,6-pentamethyl-4-piperidyl) sebacate
  - Ciba Geigy 770 - bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate

Antioxidants including

- 10
- Ciba Geigy Irganox 245 - triethylene glycol-bis-3- (3-tertbutyl-4-hydroxy-5-methyl phenyl)propionate
  - Irganox 1010 -2,2-bis[[3-[3,4-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl 3,5-bis(1,1-dimethyl ethyl)-4-hydroxy benzene propanoate
  - Irganox 1076 - octadecyl 3-(3',5'-di-tert-butyl(-4'- hydroxyphenyl) propionate

15 Anticolouring agents including

- 9, 10 dihydro-9-oxa-10-phosphaphenanthrene-1-oxide

Cure modifiers including

- 20
- Dodecyl mercaptan
  - Butyl mercaptan
  - Thiophenol
  - Nitroso compounds such as Q1301 from Wako
  - Nofmer from Nippon Oils and Fats

25 Other monomeric additives can be present in amounts up to 10% by weight as viscosity modifiers, and include monomers such as methacrylic acid, vinyl silanes, and other functional monomers. Other monomeric additives may be included to improve processing and/or material properties, these include:

- 30
- methacrylic acid, maleic anhydride, acrylic acid
  - adhesion promoters/modifiers such as Sartomer 9008, Sartomer 9013, Sartomer 9015 etc.
  - dye-enhancing, pH-adjusting monomers like Alcolac SIPOMER 2MIM
  - a charge-reducing cationic monomer to render the material more antistatic, example Sipomer Q5-80 or Q9-75



- 5        - mould release agents such as Phosphoric acid esters, e.g. octyl acid phosphate, etc, Alkyl quaternary ammonium salts, e.g. cetyl trimethyl ammonium bromine, etc., Zonyl Series, e.g. Zonyl FSO 100, Zonyl FSN 100, etc., Zelec Series, e.g. Zelec DP, Zelec UN, etc., and Unidain DS Series, e.g. DS 401, DS 202, etc.

10        The crosslinkable polymeric casting composition according to the present invention may be utilised in the preparation of an optical article. The optical article may be characterised by having an increased very high refractive index and Abbe number relative to known prior art articles. The optical article may exhibit excellent colour and low density.

      In a preferred aspect of the present invention there is provided a method for preparing a polymeric article which method includes providing

15        a cross-linkable polymeric casting composition including an effective amount of

- 20        A:        an acrylic or methacrylic monomer which provides high rigidity and low colour dispersion (High Abbe number) to the final product;
- B:        a di- or polythio compound;
- C:        a di- or polyvinyl monomer; and optionally
- D:        a polymerisable comonomer; and
- a heat and/or UV curing agent;

25        mixing the polymeric casting composition and curing agent; and  
      subjecting the mixture to a cross-linking step.

30        The casting composition may be formed into a suitable article by mixing in a convenient vessel the components making up the material, and then adding the curing catalyst. The mixed material may then be degassed or filtered. As the curing time is substantially reduced, the casting process may be undertaken on a continuous or semi-continuous basis.

      In a further aspect of the present invention there is provided a polymeric article prepared by the method as described above.

      The polymeric article may be an optical article. The optical article may

provide characteristics equal to or greater than those achievable with articles made from diethylene glycol bis(allyl carbonate) but with a considerably reduced cure time and substantially increased throughput. The optical article may be further characterised by having reduced weight and/or thickness relative to the prior art, excellent optical properties provided by the high rigidity, high Abbe number, very low Yellowness Index and low density, whilst retaining good abrasion resistance and impact resistance.

The overall refractive index may be in the high to very high refractive index range of approximately 1.58 to 1.70, preferably 1.59 to 1.65.

Accordingly in a further preferred aspect of the present invention there is provided an optical article having a high Abbe number and high to very high refractive index in the range of from approximately 1.58 to 1.70 prepared from a cross-linkable polymer casting composition including an effective amount of

- A: an acrylic or methacrylic monomer which provides high rigidity and low colour dispersion (High Abbe number) to the final product;
- B: a di- or polythio compound;
- C: a di- or polyvinyl monomer; and optionally
- D: a polymerisable comonomer.

The optical articles prepared by the method of this invention include camera lenses, ophthalmic lenses and video discs.

The present invention will now be more fully described with reference to the accompanying examples. It should be understood, however, that the description following is illustrative only and should not be taken in any way as a restriction on the generality of the invention described above.

EXAMPLE 1

A cross-linkable casting composition having the following components was prepared

		<u>Percent</u>
5	• Diacryloyl oxymethyl tricyclodecane (DCPA)	32
	• 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol (MDO)	31
	• Divinyl Benzene	21
	• Pentaerythritol tetracrylate (PTA)	16
10		<hr/> 100

The monomer mix was prepared in a beaker together with any suitable free radical initiator, for example 1.0% Trigonox TX29.

The casting material was used to fill the space between a pair of glass moulds separated by a plastic gasket at their periphery and held together by a clip. Cure time was 8 hours with heating at a temperature of 40 to 120°C. A satisfactory lens having a high Abbe number of 42 and high refractive index was formed.

EXAMPLES 2 TO 28 AND COMPARATIVE EXAMPLES 1 TO 3

The procedure of Example 1 was repeated utilising the components set out below. Results are given in Tables 1 and 2 below.

TABLE 1

Formulations												Properties		
No.	DCPA	PTA	DCPM	A9300*	DVB	MDO	MMTHT	Component D	Epoxy Compound	RI	Abbe No.	Tg (°C)		
1.	32	16			21	31				1.60	42	90		
2.	32	11			26	31				1.60	41	94		
3.	46				27	27				1.60	41	103		
4.	43				28	29				1.60	40	91		
5.	15	32			22.5	30.5				1.60	41	108		
6.	15	33			22	30				1.60	41	104		
7.	45				25	25		3** (ATM20)	2*** (Epolight 100MF)	1.60	40	-		
8.	32	14			23	31				1.60	41	91		
9.	39	10			20		31			1.59	42	113		
10.	47				26	27				1.60	41	100		
11.	35			18	14	33				1.60	42	67		
12.	41.5	2.5			27	29				1.60	40	92		

Table 1 continued

Formulations											Properties		
No.	DCPA	PTA'	DCPM	A9300*	DVB	MDO	MMTHT	Component D	Epoxy Compound	RI	Abbe No.	Tg (°C)	
13	37	7.5			25.5	30				1.60	40.5	90	
14	34	10			25	31				1.60	41	88	
15	34	15.5			20.5	30				1.60	42	89	
16	35	16			17	32				1.60	42.5	75	
17	30.5	19			19.5	31				1.59	42	90	
18	15	32			22		31			1.60	42.5	80	
19		45			22	33				1.60	40.2	90	
20	48				24.5	27.5				1.60	41.5	90	
21			43.5		26.5	30				1.60	39.5	88	
22	20	15			33	32				1.607	38.3	108	
23	32				36	27		5****(9G)		1.602	38.5		
24	10	25			30	35				1.608	38.5	102	
25		40			20	40				1.606	40	78	

Formulations										Properties		
No.	DCPA	PTA	DCPM	A9300*	DVB	MDO	MMTHT	Component D	Epoxy Compound	RI	Abbe No.	Tg (°C)
26		35	7		20	38				1.604	40.4	
27	22.5	17.5			25	35				1.605	39.5	78
28	16	24			25	35				1.604	39.6	90

\* A9300 = tris-hydroxyethyl isocyanurate triacrylate

\*\* ATM20 , = ethoxylated bis-phenol A dimethacrylate

\*\*\*Epolight 100MF =  $\text{CH}_3\text{---CH}_2\text{---C}(\text{CH}_2\text{---O---CH}_2\text{---CH---CH}_2)_3$

\*\*\*\*NK Ester 9G = polyethylene glycol dimethacrylate

DCPM = Dimethyloltricyclodecane dimethacrylate

TABLE 2

Formulations								Properties		
No.	DVB	TMPT	PETP	BMME	PETG	DME	MDO	RI	Abbe No.	Tg (°C)
1	35						65	1.66	29	<30
2	70				25	5		1.614	31	
3	70		20	10				1.625	30	

TMPT = trimethylolpropane tris( $\beta$ -thiopropionate)  
 PETP = pentaerythritol tetrakis ( $\beta$ -thiopropionate)  
 BMME = 1,4-bis (mercaptomethyl) benzene  
 PETG = pentaerythritol tetrakis ( $\beta$ -thioglycolate)  
 DME = 1,2-dimercaptoethane

Finally, it is to be understood that various other modifications and/or alterations may be made without departing from the spirit of the present invention as outlined herein.



Claims

1. A cross-linkable polymeric casting composition including an effective amount of

A: an acrylic or methacrylic monomer which provides high rigidity and low colour dispersion (High Abbe number) to the final product;

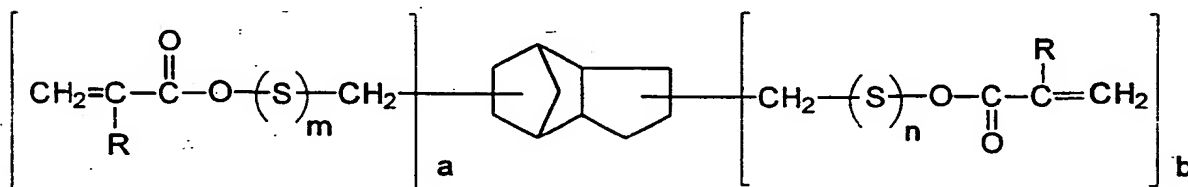
B: a di- or polythio compound;

C: a di- or polyvinyl monomer; and optionally

D: a polymerisable comonomer.

2. A cross-linkable polymeric casting composition according to Claim 1, wherein component A is selected from acrylates or methacrylate derivatives of a cycloolefin.

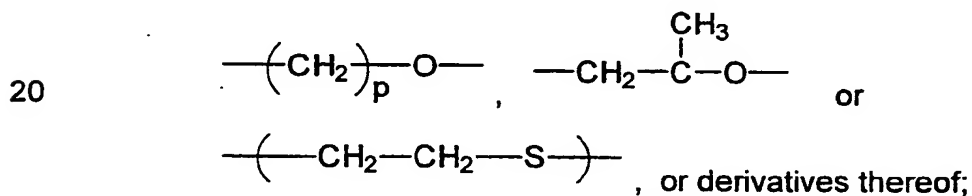
3. A cross-linkable polymeric casting composition according to Claim 2, wherein the acrylate or methacrylate derivative is of the formula



where R can be H or CH

a = 1-3, b = 1-3, m = 0-6, n = 0-6.

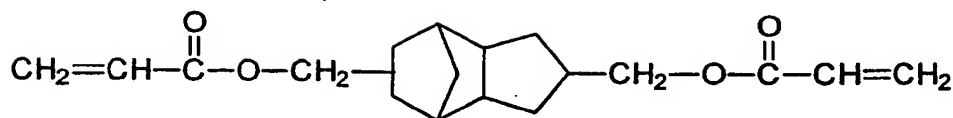
S is a spacer group selected from one or more of the following



wherein p = 1-4

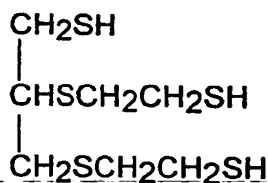
4. A cross-linkable polymeric casting composition according to Claim 3 wherein the acrylate or methacrylate derivative is a tricyclodecane dimethanol acrylate of the following formula

24

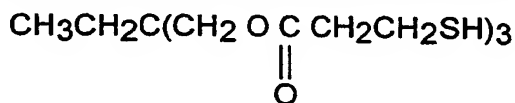


5. A cross-linkable polymeric casting composition according to Claim 1 wherein component A is a highly rigid, high Abbe No. polyfunctional acrylate or methacrylate.
- 5 6. A cross-linkable casting composition according to Claim 5, wherein component A is a pentaerythritol tetracrylate.
7. A cross-linkable polymeric casting composition according to Claim 1 wherein component A is present in amounts of from approximately 20 to 60% by weight based on the total weight of the casting composition.
- 10 8. A cross-linkable polymeric casting composition according to Claim 7, wherein component A is present in amounts of from approximately 30 to 55% by weight, based on the total weight of the casting composition.
9. A cross-linkable polymeric casting composition according to Claim 1, wherein component B is a di-, tri- or tetra- polythiol compound.
- 15 10. A cross-linkable polymeric casting composition according to Claim 9, wherein the polythiol is selected from one or more of the following:

(a) 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol [MDO]

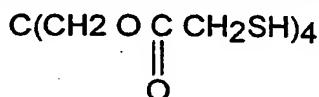


(b) Trimethylolpropane Tris (3-mercaptopropionate) [TTMP]



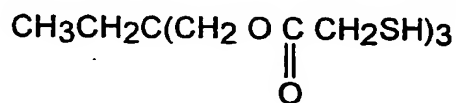
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(c) Pentaerythritol Tetrakis (3-mercaptoproacetate) [PTMA]

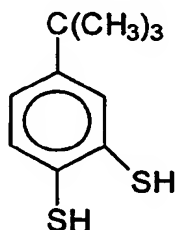


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- (d) Trimethylolpropane Tris (3-mercaptoacetate) [TTMA]



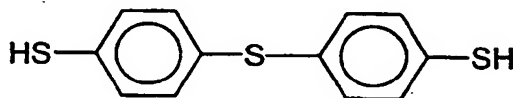
- (e) 4-t-butyl-1,2-benzenedithiol



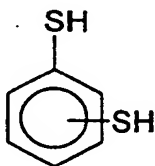
- 5 (f) Bis(2-mercaptoethyl)sulfide



- (g) 4,4'-thiodibenzenethiol

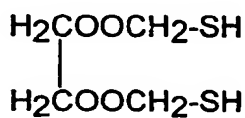


- (h) benzenedithiol

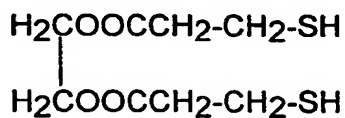


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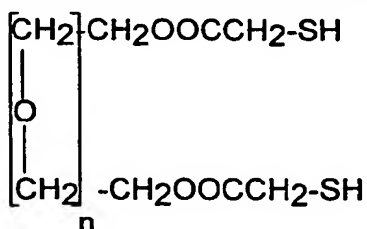
- (i) Glycol Dimercaptoacetate



- (j) Glycol Dimercaptopropionate Ethylene bis(3-Mercaptopropionate)

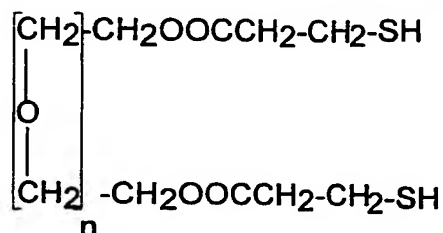


- 15 (k) Polyethylene Glycol Dimercaptoacetates

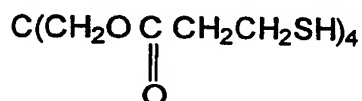


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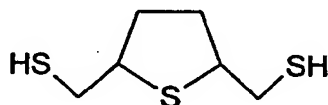
- (l) Polyethylene Glycol Di(3-Mercaptopropionate)



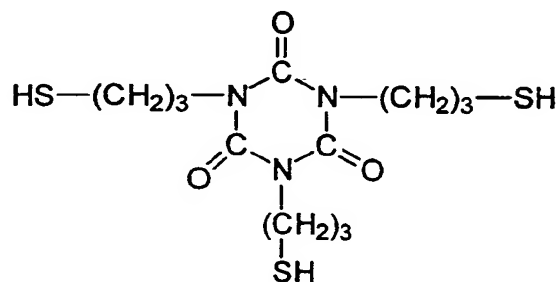
- (m) Pentaerythritol Tetrakis (3-mercaptopropionate) [PTMP]



- 5 (n) Mercapto-methyl tetrahydrothiophene [MMTHT]



- (o) Tris-(3-mercaptopropyl)isocyanurate [TMPIC]

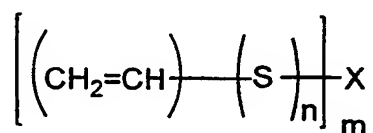


11. A cross-linkable polymeric casting composition according to Claim 10 wherein the polythiol is 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol [MDO].

12. A cross-linkable polymeric casting composition according to Claim 10, wherein component B is present in amounts of from approximately 15 to 60% by weight, based on the total weight of the casting composition.

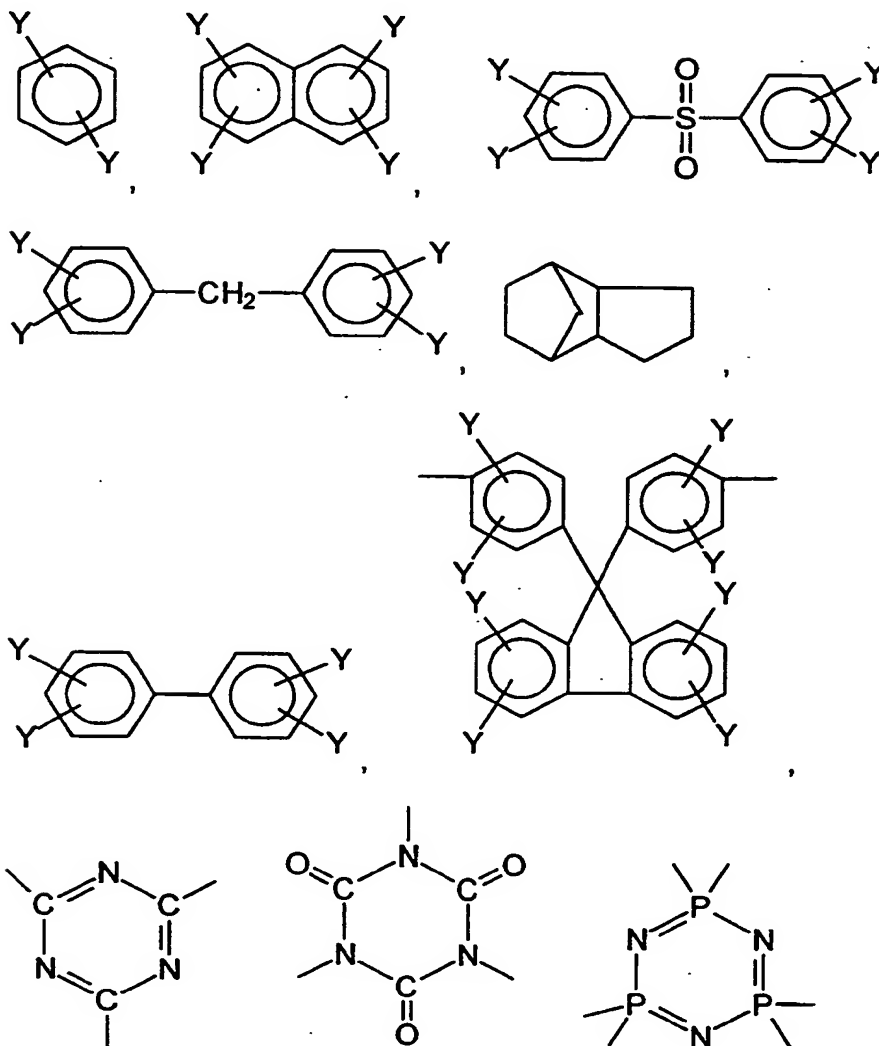
13. A cross-linkable polymeric casting composition according to Claim 12, wherein component B is present in amounts of from approximately 20 to 55% by weight, based on the total weight of the casting composition.

14. A cross-linkable polymeric casting composition according to Claim 1, wherein component C is a rigid cyclic vinyl monomer of the formula



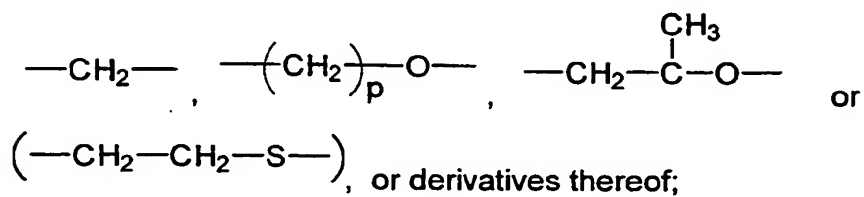
wherein

X is selected from one or more of the following



5

S is a spacer group selected from one or more of the following



10

Y is hydrogen or halogen

$n = 0, 1 \text{ or } 2$

$m = 2 - 6$

$p = 1 - 4$

15. A cross-linkable polymeric casting composition according to Claim 14, wherein the divinyl or polyvinyl monomer is an aromatic divinyl monomer selected from the group consisting of divinyl benzene, divinyl naphthene or derivatives thereof.
- 5 16. A cross-linkable polymeric casting composition according to Claim 14, wherein component C is present in amounts of from approximately 5 to 50% by weight, based on the total weight of the casting composition.
17. A cross-linkable polymeric casting composition according to Claim 16, wherein component C is present in amounts of from approximately 15 to 40% by weight, based on the total weight of the casting composition.
- 10 18. A cross-linkable polymeric casting composition according to Claim 1, wherein component D is an unsaturated or epoxy comonomer selected from the group consisting of methacrylates, acrylates, vinyl, vinyl ethers, allyls, epoxides and mixtures thereof.
- 15 19. A cross-linkable polymeric casting composition according to Claim 18, wherein component D is an epoxidised monomer or oligomer selected from the group consisting of internal, terminal, mono-functional, di-functional, tri-functional, tetra-functional, aliphatic, aromatic, cyclic, structurally simple, structurally complex, esters, ethers, amines, or mixtures thereof.
- 20 20. A cross-linkable polymeric casting composition according to Claim 19, wherein the epoxidised monomer or oligomer is present in amounts of from approximately 0.001% to 10% by weight, based on the total weight of the casting composition.
- 25 21. A method for preparing a polymeric article, which method includes providing
- a cross-linkable polymeric casting composition including an effective amount of
- A: an acrylic or methacrylic monomer which provides high rigidity and low colour dispersion (High Abbe number) to the final product;
- B: a di- or polythio compound;
- C: a di- or polyvinyl monomer; and optionally
- 30

D: a polymerisable comonomer; and  
a heat and/or UV curing agent;

mixing the polymeric casting composition and curing agent; and  
subjecting the mixture to a cross-linking step.

5 22. A method according to Claim 21, wherein the polymeric article is an optical article.

23. An optical article having a high rigidity, high Abbe number and high to very high refractive index in the range of from approximately 1.58 to 1.70 prepared from a cross-linkable polymer casting composition including an effective  
10 amount of

A: an acrylic or methacrylic monomer which provides high rigidity and high Abbe number to the final product;

B: a di- or polythio compound;

C: a di- or polyvinyl monomer; and optionally

15 D: a polymerisable comonomer.

24. An optical article according to Claim 23, wherein the optical article further exhibits a very low Yellowness Index and low density.

25. A cross-linkable polymeric casting composition substantially as hereinbefore described with reference to any one of the examples.

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/AU 96/00314

## A. CLASSIFICATION OF SUBJECT MATTER

Int Cl<sup>6</sup>: C08F 220/20, 220/28, 220/38, 212/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC C08F 20/20, 20/28, 20/38, 12/34, 12/36, 220/20, 220/28, 220/38, 212/34, 212/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
AU : as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
DERWENT : thio : or mercapt :

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU, A, 50581/93 (SOLA INTERNATIONAL HOLDINGS LTD.) 26 May 1994 pages 6 and 7 and Examples 11, 12, 13 and 14	1, 5, 7-10, 12, 13, 21-24
X	AU, B, 44089/89 (616064) (SHOWA DENKO KABUSHIKI KAISHA) 14 May 1990 Examples 26, 34, 35, 36	1, 5, 7-9, 21-23
X	Derwent Abstract Accession No. 95-118718/16, Class A14, JP, A, 07041520 (MITSUBISHI PETROCHEMICAL CO LTD) 10 February 1995 Abstract	1, 7, 9, 21, 22

☐ Further documents are listed in the continuation of Box C

☐ See patent family annex

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance  
"E" earlier document but published on or after the international filing date  
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
"O" document referring to an oral disclosure, use, exhibition or other means  
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  
"&" document member of the same patent family

Date of the actual completion of the international search  
7 June 1996

Date of mailing of the international search report

19TH JUNE 1996.

Name and mailing address of the ISA/AU  
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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 96/00314

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No 93-131324/16, Class P81, JP, A, 05070524 (NIPPON OILS & FATS CO LTD) 23 March 1993 Abstract	1, 5, 9, 10, 12, 13
X	Derwent Abstract Accession No 92-101772/13, Class P81, JP, A, 4045-401 (MITSUBISHI GAS CHEM KK) 14 February 1992 Abstract	1, 5, 9, 12, 13
X	Derwent Abstract Accession No 94-186824/23, Class P81, JP, A, 06123855 (TOKYO KEIKAKU KK) 6 May 1994 Abstract	1, 5, 9, 12, 13

# INTERNATIONAL SEARCH REPORT

## Information on patent family members

International Application No.  
**PCT/AU 96/00314**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
AU	44089/89	DE	68917908	EP	394495	JP	2113005
		US	5183917	US	5270439	WO	9004587
		JP	2113027	JP	2160762	JP	3021638
		JP	3054226				
AU	50581/93	CA	2102378	EP	598552	JP	7002939
		US	5502139				